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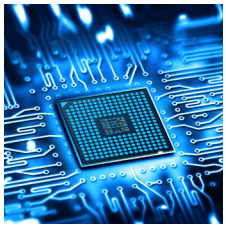
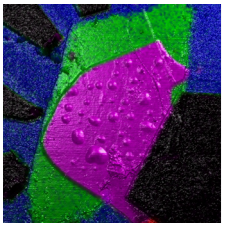
AFM-Raman

Colocalized AFM-Raman Analysis of 2D Materials Heterostructures





Application Note

2D-Materials AFM26

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Abstract: This application note reports on colocalized AFM-Raman measurements of vertical Van der Waals heterostructures of 2D materials: hBN/graphene/WSe_2 and hBN (3-5 nm)/bilayer graphene/hBN/graphite gate/hBN/SiO_2/Si. Topographic, contact potential difference, and Raman data are generated on the same location with the same tip using a fully integrated AFM-Raman microscope, the new SignatureSPM. The enhanced confidence in data provided by the true colocalization of chemical, electronic, and physical properties, combined with its compactness and user-friendliness, makes SignatureSPM an indispensable tool for researchers working on the development of nanodevices based on 2D materials.

Keywords: Transition metal dichalcogenides, heterostructure, graphene, 2D materials, h-BN, nanodevices, AFM, colocalized AFM-Raman, correlative data, Raman spectroscopy

Introduction

Two-dimensional (2D) materials are a class of ultrathin materials comprising just a single or a few layers of atoms, exhibiting extraordinary electronic, mechanical, and optical properties that distinguish them from their three-dimensional counterparts. With their versatility and tunable properties, 2D materials present vast potential for applications spanning flexible electronics, photonic devices, energy storage, and catalysis, revolutionizing industries and shaping the future of advanced technologies [1].

Two-dimensional (2D) materials encompass a range of conductive (graphene, MXenes…), semiconducting (transition metal dichalcogenides (TMD)), and dielectric (h-BN) materials critical for realizing electronic and optoelectronic devices. In essence, 2D materials cover all key elements needed for constructing modern electronic and optoelectronic systems. While creating vertical and horizontal heterostructures, interactions between atomic layers dramatically change the properties and induce phenomena with characteristics distinct from its constituent parts. Engineering layer–layer interactions (electron-electron, electron-phonon…) provides a powerful way to realize novel and designable quantum phenomena in Van der Waals heterostructures [2].

Raman spectroscopy is considered as an essential tool for characterizing 2D materials [3]. Raman spectroscopy probes the lattice vibrational modes that impact the electronic response of a heterostructure by affecting electron-phonon interlayer interactions. Raman spectroscopy also provides information about layer thickness, strain, and presence of defects [4]. To cite an example, Jin *et al* [5] have reported an interlayer electron–phonon interaction in WSe_2/hBN heterostructures, where optically silent hBN phonons emerge in Raman spectra with strong intensities through resonant coupling to WSe_2 electronic transitions. **AFM analysis** contributes significantly to the characterization of 2D materials heterostructures by providing layer thickness, electrical properties, and presence of defects/grain boundaries.

Jointly collecting AFM and Raman data would be a great leap forward in understanding the structural and electronic properties of TMD layers and their heterostructures and thereby addressing issues related to defects, doping, and interlayer interaction.

In this application note, results from the analysis of a **hBN/Graphene/WSe_2 vertical heterojunction** and a **graphite gate/hBN/bilayer graphene/hBN device structure** by an **AFM-Raman SignatureSPM** microscope will be presented.

Experiment and Results

Colocalized AFM-Raman measurements have been carried out on a hBN/graphene/WSe_2 heterojunction transferred on SiO_2/Si substrate with gold contacts (courtesy of Y. Gallais & M.L. Della, MPQ, Paris City University, France) and on a hBN(3-5 nm)/bilayer graphene/hBN/graphite gate/hBN heterostructure on SiO_2/Si (courtesy of P. Stepanov, A. Reserbat-Plantey, F. Koppens, ICFO).

The analysis was performed using an AFM-Raman **SignatureSPM** system from HORIBA which is a **fully integrated** atomic force microscope (SmartSPM) with a Raman microscope. The **SignatureSPM** instrument is

shown in Fig. 1. The 532 nm *p*-polarized excitation laser is brought to the sample in normal incidence through a 100× NA 0.7 WD objective. The outgoing Raman signal is backscattered and collected through the same path before reaching a three-grating (150 gr/mm, 600 gr/mm, 1800 gr/mm) spectrometer via optical fiber coupling. The laser beam is focused onto an ACCESS-EFM tip from App Nano. This probe is a sharp silicon cantilever-based tip with a conductive Ir-Pt coating for Kelvin and electric force modes. The "ACCESS" design allows a direct optical view of the AFM tip for applications that require seeing the tip as it engages the surface. All "ACCESS" type tips are best suited for colocalized measurements as they ensure easy Raman laser-tip visual alignment.

Figure 1 Picture of the SignatureSPM instrument: a compact multimodal AFM-Raman characterization platform.

Navigation across the sample to reach the region of interest (ROI) (e.g. the region featuring the hBN/Graphene/WSe_2 flakes) is made possible with the top camera optical view. The optical image in Fig. 2 displays the ROI with two distinct colored flakes surrounded by gold contact pads. The tip apex-Raman laser spot alignment is performed visually by looking at the top camera optical view and moving in x,y directions on the SPM using two mechanical screws. The laser focus is adjusted using the knob moving in z direction of the x100 objective and eventually by maximizing the sample signal. An AFM scan was acquired at 0.2 Hz with a resolution of 512 lines. A 35 µm × 35 µm Raman map (150 px × 150 px) was collected with a laser power of 17.5 mW, a 600 gr/mm grating, an acquisition time/px of 50 ms, and a pixel size of 230 nm. The topographic (a) and color-coded Raman (b) maps are displayed in Fig. 3 together with the overlay of the Raman map on the 3D topographic map (c) and the reference spectra defining the color code of the Raman map (d). The hyperspectral Raman dataset was statistical analyzed by CLS (classical least square) fitting using five reference spectra averaged from 25 pixels. Five areas were clearly distinguished based on the chemical differences: **contact pads** (no signal), **Silicon** (LO band at 520.8 cm^{-1}) outside of the flakes, outer of the **h-BN** (E_{2g} band at 1364 cm^{-1}) flake, central **graphene** (2D band at 2716 cm^{-1}) flake, and uncovered **WSe_2** (E^1_{2g} band at 248 cm^{-1}). Let's note that higher intensity of the 2D band can be seen on the bubbles observed on the AFM topographic image. Additional mapping in the frequency modulated Kelvin mode was acquired. The second derivative of capacitance ($\partial^2C/\partial z^2$) and contact potential difference maps are shown in Fig. 4. A good correlation can be observed between the topography and the Kelvin mode responses.

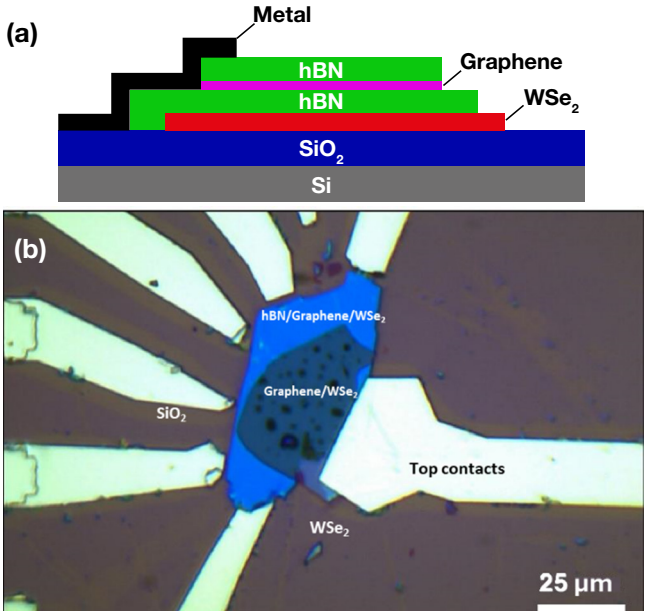

Figure 2: (a) schematic diagram of the heterostructure, (b) 180 µm × 120 µm optical image from the top camera of the Signature SPM with 100× objective.

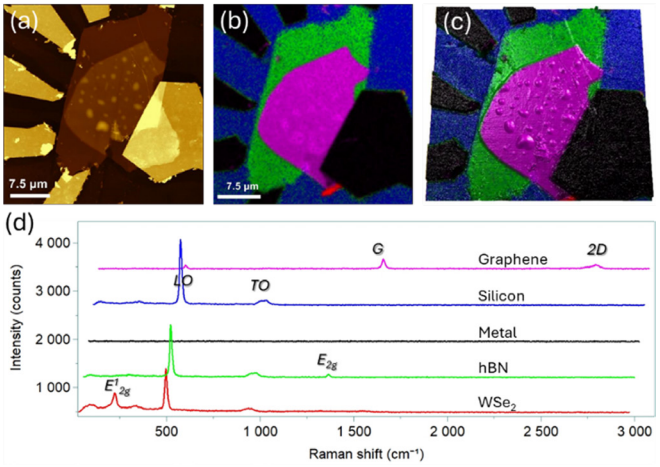

*Figure 3: (a) Topographic image, (b) Color-coded Raman image (see (d)), (c) Overlay of color-coded 35 µm × 35 µm Raman image on 3D topographic image, (d) Raman spectra from **red WSe_2**, **pink graphene**, **green hBN**, **blue silicon** and **black gold contact areas** of the Raman map. The spectra are shifted in the wavenumber x axis for better visibility.*

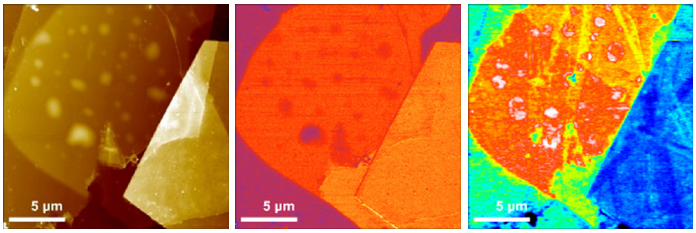

Figure 4: Topographic image, second derivative of capacitance ($\partial^2C/\partial z^2$) and contact potential difference image in force modulated Kelvin mode.

The second sample, graphite gate/hBN/bilayer graphene/hBN was analyzed following the same experimental workflow: navigation to find the ROI using camera top view, tip-laser alignment, AFM scan, Raman mapping. The AFM scan was acquired at 1 Hz with a resolution of 512 lines. A 20 µm × 10 µm Raman map (80 px × 40 px) was collected with a laser power of 17.5 mW, a 1800 gr/mm grating, an acquisition time/px of 1 s, and a pixel size of 250 nm. The topography, the contact potential difference, the Raman map upon CLS fitting and the reference spectra are displayed in Fig. 5.

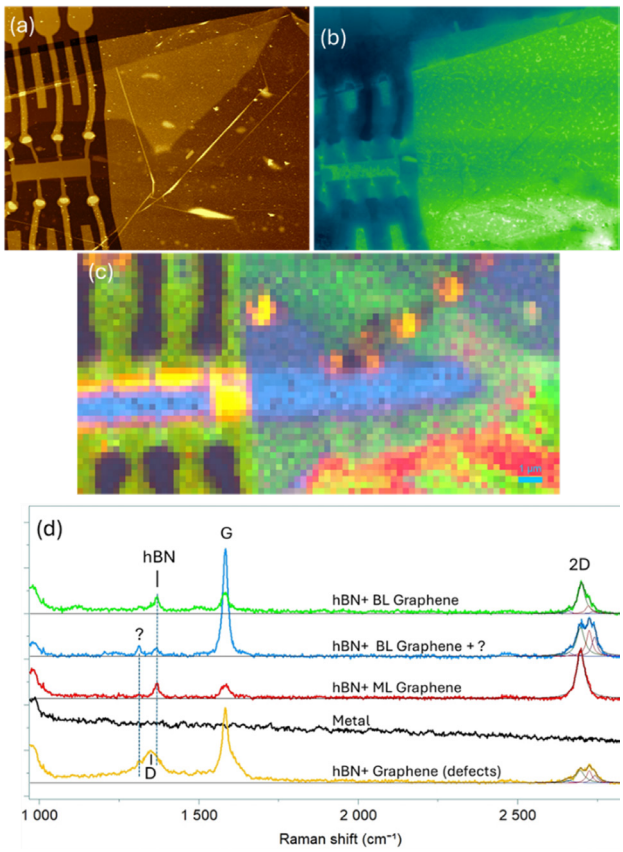

Figure 5: (a) Topographic image, (b) Contact potential difference image in amplitude modulated Kelvin mode, (c) Raman map acquired inside (a) (location is shown as a white rectangle in (a)) and displayed upon CLS fitting using reference spectra shown in (d).

Conclusions and perspectives

Two vertical Van der Waals heterostructures of 2D materials, hBN/Graphene/WSe_2 and graphite gate/hBN/bilayer graphene/hBN have been characterized by an **AFM-Raman SignatureSPM** system. Such heterostructures present exciting possibilities for developing advanced electronic devices with improved efficiency, functionality, and adaptability compared to traditional semiconductor technologies. True colocalized maps of topography, contact potential difference and Raman signal have been obtained. Such maps allow us to unambiguously identify the location of each material stack, know its CPD response, and check on the presence of topographic defects (wrinkles, bubbles). Such correlative SPM, photoluminescence (not shown here) and Raman data are the way to characterize electron-phonon interlayer interactions and explain novel quantum phenomena.

SignatureSPM is bound to become an invaluable asset for researchers in the field of 2D materials-based nanodevices. Its ability to provide precise data through the colocalization of chemical, electronic, and physical properties, along with its user-friendly design, makes it a go-to tool for accurate and reliable results.

Acknowledgments

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